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Modelling of the steel–concrete interface to obtain information on reinforcement bar corrosion

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Abstract

The selection of an equivalent circuit that faithfully models the steel–concrete interface response to the application of electrical signals is a fundamental aspect of the electrochemical determination of reinforcement corrosion rate. Experimental evidence is provided in favour of using a modified Randles circuit in which the corroding interface is characterised by a parallel combination of a constant phase element and a charge transfer resistance in series with a Warburg element. An advantage of having an appropriate model of the steel–concrete system is the possibility of carrying out studies of quality of the information that is extracted from the experimental data. A sensitivity-algorithm is applied with the object of identification of the conditions in which the system's response is dominated by certain parameters or combinations of them.

1. Introduction

Degradation of reinforced concrete structures is a matter of great practical importance. Problems are often related to the corrosion of steel reinforcement bars. In such cases, corrosion rate determinations can facilitate estimations of the progress of deterioration and residual lifetime predictions [1–4].

For some time, electrochemical methods have been used to obtain corrosion rate measurements. In particular, estimations based on the Stern–Geary equation have proven to be very useful [5]

$$i_{corr} = B/R_t, \qquad (1)$$

where B = constant and R_t = charge transfer resistance of the corrosion process.

Several laboratory and field techniques are used with reinforced concrete specimens and structures to obtain the value of R_t [6–8]. The greatest errors in its determination are often due to an erroneous interpretation of the system response to the application of electrical signals in the time and frequency domains. A fundamental aspect in the calculation of R_t is the selection of a model (equivalent electrical circuit) of the system that faithfully reflects its response [9–11].

The simplified Randles circuit in Figure 1(a) is very often used to describe the electrochemical system in reinforced concrete owing to the simplicity of data analysis [12]. However, the disadvantage is that at times it diverges excessively from the real response of the steel–concrete system [11]. A model consisting of a series of resistor–capacitor pairs, like that in Figure 1(b), fits this response much better [13–15], though in this case the high number of parameters can make it difficult to locate the true value of R_t. Another approach adopted in some studies [16–18] is to replace the capacitance C in the Randles model with a constant phase element, CPE (Figure 1(c)). Unfortunately, the introduction of a CPE greatly complicates the method of calculating R_t in the time domain. It is much easier to analyse the system's response (and to calculate R_t) in the frequency domain. However the longer time necessary to make the measurements in this domain, the greater cost of the experimental equipment and its worse adaptation to field measurements can make it advisable to operate in the time domain. More general than the preceding models, but also mathematically more complex, is that of Figure 1(d), which includes both CPE and diffusion effects.

Sagüés et al. [16] and Birbilis et al. [17] have proposed numerical calculation procedures for analysing the response in the time domain of the model in Figure 1(c). For the model in Figure 1(d), the presence of the diffusion element Z_w further complicates the problem of obtaining the circuit parameters from the potential-time data. The recent development by Feliu et al. [18] of a

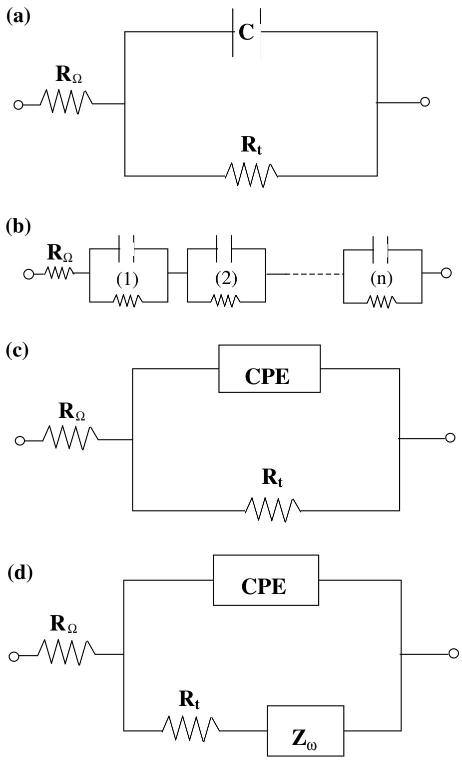

Fig. 1. Equivalent circuits considered. R_Ω = ohmic resistance, R_t = charge transfer resistance, C = capacitance, CPE = constant phase element, Z_w = Warburg diffusion.

computational algorithm for fitting the response of the latter model to the experimental data has provided the necessary calculation tool to check its capacity to interpret the behaviour of the steel–concrete system.

The fundamental objective of this work is to provide experimental evidence in favour of using the circuit in Figure 1(d) to analyse the time response of the steel–concrete system to electrical signals. The effect of the model's structure on the precision with which their parameters are determined is also considered.

2. Computation and experimental procedure

The applicability of the circuit in Figure 1(d), which is henceforth referred to as the R_t/CPE/W circuit, has been studied with our own data, obtained using the experimental technique reported previously [10–12], and with data from the literature, which has the advantage of reflecting a wide variety of experimental situations, thus allowing the conclusions to be of a more general character.

In the calculations the effect of the CPE has been represented by the expression:

$$Z_{\mathrm{CPE}} = 1/Y_{\mathrm{o}}(j\omega)^{\beta}, \tag{2}$$

where Z_{CPE} = impedance of the CPE; Y_{o} and β = constant parameters; ω = angular frequency; and $j = \sqrt{-1}$.

Since the testing conditions with reinforced concrete favour a semi-infinite diffusion process [10–12], the effect of diffusion has been represented by

$$Z_{\mathrm{w}} = \sqrt{2}\sigma/\sqrt{j\omega}, \tag{3}$$

where Z_{w} = Warburg impedance and σ = Warburg coefficient.

The extraction of the parameters of the R_t/CPE/W circuit from the response curves has been carried out by means of the algorithm developed in [18], whose fundamentals are summarised in the Appendix A. The input data for the calculation programme consists of the series of experimental potential-time points as well as the sampling period and the duration and width of the pulse.

For the experimentation in our laboratory, use was made of reinforced concrete slabs which embedded steel reinforcements of 0.8 cm in diameter and 130 cm in length [11, 12]. A standard 3-electrode set-up was used. In many of the tests the obtainment of the response to the current pulses involved the placing of a counter-electrode of 7 cm in diameter on the concrete surface. In this case, the small size of the counter-electrode compared with the length of the reinforcement bar led to a non-uniform distribution of the electric signal.

3. Demonstration of applicability

3.1. *Current steps*

The work takes into consideration five response curves of steel in concrete selected from the literature [14, 16, 19], which were obtained using the galvanostatic step technique. In the original studies these curves were

Table 1. Values of parameters for an optimum fit according to the R_t/CPE/W model

Example	Source of experimental data	Time elapsed from start of transient/s	R_t/Ω cm^2	Y_0/F s$^{\beta-1}$ cm^{-2}	β	σ/Ω cm^2 s$^{-0.5}$
A (Figure 2)	Newton and Sykes [14]	2	2.27×10^3	1.64×10^{-5}	0.95	201
B (Figure 3)	Newton and Sykes [14]	13	1.09×10^5	2.33×10^{-5}	0.75	412
C (Figure 4)	Sagüés et al. [16]	600	6.74×10^6	3.50×10^{-5}	0.76	0
			$\tau_a = Y_0 R_t/\mathrm{s}^{\beta}$	β	$\sigma/R_t/\mathrm{s}^{-0.5}$	
D (Figure 5)	Cui and Yan [19]	144	12.9	1.0	0.016	
E (Figure 6)	Cui and Yan [19]	26	0.34	0.95	0.016	
F (Figure 7)	Authors' experiments	11 (for decaying part of curve)	1.05	0.65	0.039	

analysed with different calculation techniques on the basis of various models. Now, the same curves are analysed taking the R_t/CPE/W circuit as the system model. The goodness of the fit must serve as an argument in favour of the model's validity. Evidently the values of R_t that are obtained must be in consonance with the behaviour (active or passive) or the reinforcements.

From those potential-time curves a series of points spaced regularly in time were obtained, which were entered into the aforementioned calculation programme [18]. Fitting provided the series of values of the parameters (R_t, Y_0, β and σ) shown in Table 1, which characterise the corroding interface. The R_Ω term was zero as was to be expected of data that were corrected for ohmic drop. The quality of the fit can be checked visually in the graphs in Figures 2–7, where overpotential is plotted against time. It can be seen that the calculated curves are superimposed with notable exactitude over the experimental values. In no case has the error in the fit exceeded 1–2%.

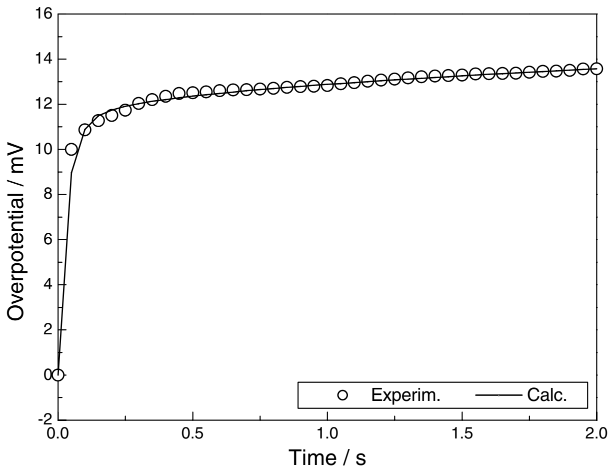

Fig. 2. Computer fit according to the R_t/CPE/W model (full line) compared with experimental values (circles). The latter taken from Figure 5 of a paper by Newton and Sykes [14].

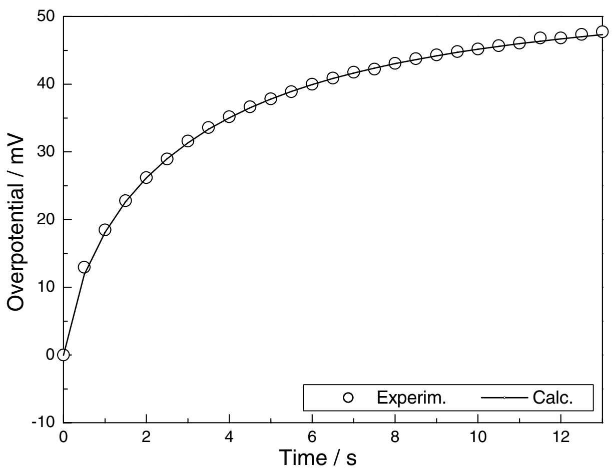

Fig. 3. As in Figure 2 but for experimental values taken from Figure 7 of a paper by Newton and Sykes [14].

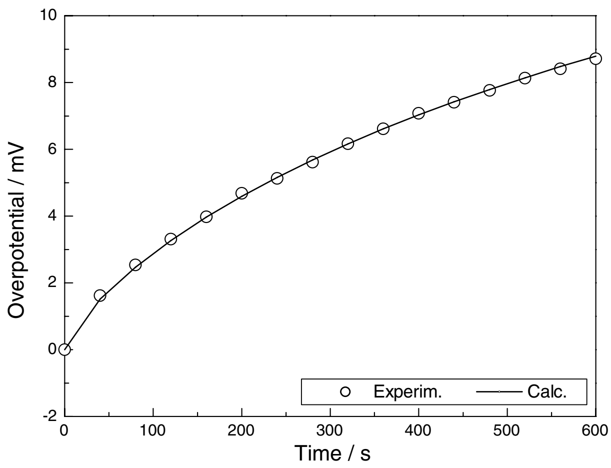

Fig. 4. As in Figure 2 but for experimental values taken from Figure 3 of a paper by Sagüés et al. [16].

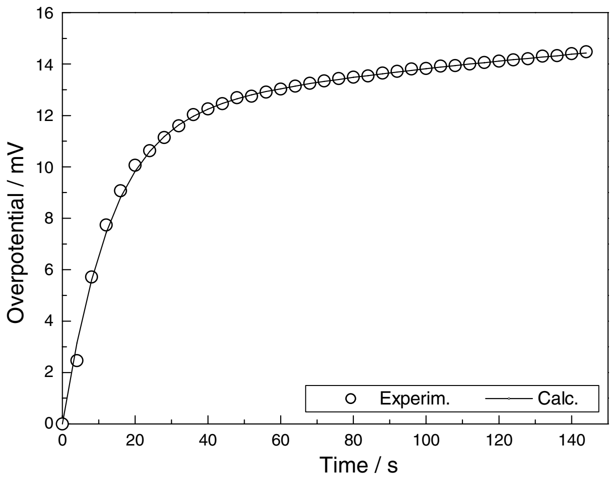

Fig. 5. As in Figure 2 but for experimental values taken from Figure 10 of a paper by Cui and Yan [19].

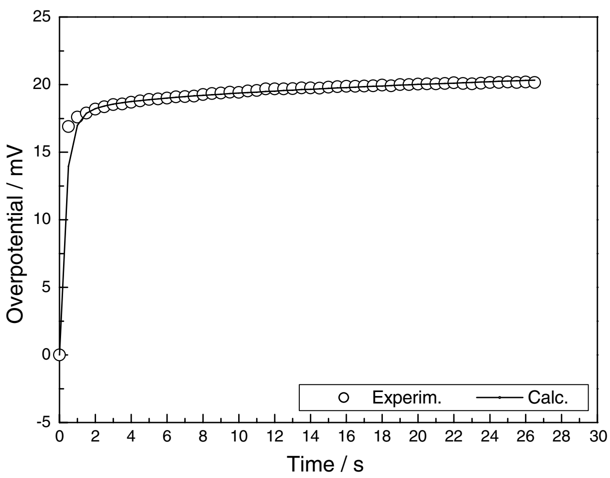

Fig. 6. As in Figure 2 but for experimental values taken from Figure 12 of paper by Cui and Yan [19].

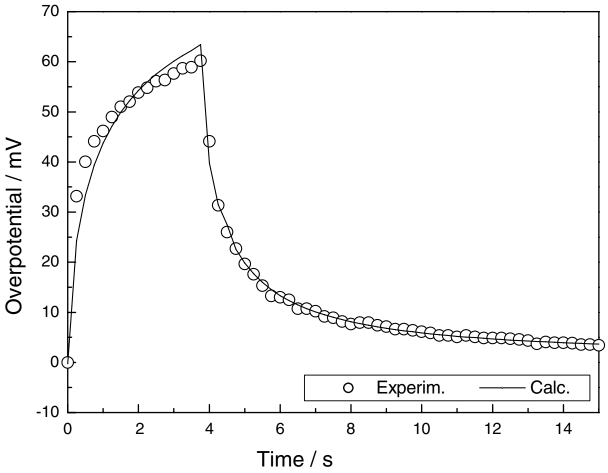

Fig. 7. As in Figure 2 but for experimental values from the authors' measurements.

In Figures 2 and 3 the experimental points have been extracted from the potential-time curves of a paper by Newton and Sykes [14] referring to steel reinforcements in active state (Figure 2) and passive state (Figure 3) embedded in concrete. Together with these points the fitted curve by assuming the R_t/CPE/W circuit is shown. The numerical analysis produced the series of values R_t, Y_o, β and σ of examples A and B in Table 1. It is not possible to establish a direct comparison between these values and those determined in [14], since the latter were calculated for an equivalent circuit with three capacitive components and three resistive components (Figure 1 (b)). Nevertheless, we note that the sum of the three separate resistive components given in the original study is equivalent to the value of R_t in Table 1, and that the sum of the inverse values of the capacitive components, excluding the component of the smallest magnitude, is approximately equivalent to $1/Y_o$.

The experimental points in Figure 4 have been deduced from a paper by Sagüés et al. [16]. As before, the calculated curves closely match the experimental curves. The fit parameters of the R_t/CPE/W circuit (example C in Table 1) practically coincide with the values that were obtained in [16] for a circuit such as that shown in Figure 1(c), in which the diffusion effect is supposed to be negligible. The magnitude of the value of R_t is typical of the passive behaviour of the galvanised steel rebars in concrete that were used in [16].

Finally, the experimental points in Figures 5 and 6, for passive and active steel reinforcements, respectively, were extracted from the galvanostatic curves of a paper by Cui and Yan [19] (examples D and E in Table 1). Here too the response of the R_t/CPE/W circuit is fitted quite satisfactorily to the shape of these curves. Since the cited work does not mention the exact magnitude of the current step applied, it is not possible to refer the values of R_t and Y_o to the unit of reinforcement surface area; instead the value of the apparent time constant $\tau_a = Y_o R_t$ has been calculated, which is independent of the surface area. These values (Table 1) agree reasonably well with the values of τ_a that are deduced from the values of R_t and Y_o in [19]. They also concord with the typical values for passive reinforcements in a chloride-free concrete and active rebars in a concrete with chlorides.

3.2. *Galvanostatic pulses*

In addition to current steps, the application of current pulses of a finite duration [11, 12] is habitual practice in laboratory tests and on site measurements aimed at obtaining information on the corrosion rate of reinforcements in concrete. Figure 7 shows one of the transients thus obtained in our laboratory. The representation log η vs t, being η = overpotential and t = time after current interruption, shows a clear non-exponential behaviour for the decaying part of the curve (Figure 8); instead of the theoretical straight line from the simplified Randles circuit, a curved line appears whose slope depends on the point of the curve that is selected, for instance, after 0.5 s the slope is some two times greater than after 2 s, and some six times greater than after 10 s. However, this behaviour is perfectly compatible with a system represented by the R_t/CPE/W circuit, as is confirmed in Figure 7, where the curve calculated for the response of this circuit is fitted with little error to the experimental points along the decaying part of the curve. Since the area of the reinforcements affected by the electric current injected from a counter-electrode of a much smaller size than the reinforcements is not known, the calculated parameters cannot be referred to the unit of surface area, though they allow the value of τ_a to be calculated (example F in Table 1). This value is in agreement with the state of corrosive activity foreseeable for a steel embedded in concrete with 3% chloride as in the case of the example.

4. Use of the model

As has been seen in the above examples, it is possible to quite satisfactorily fit the R_t/CPE/W circuit to the

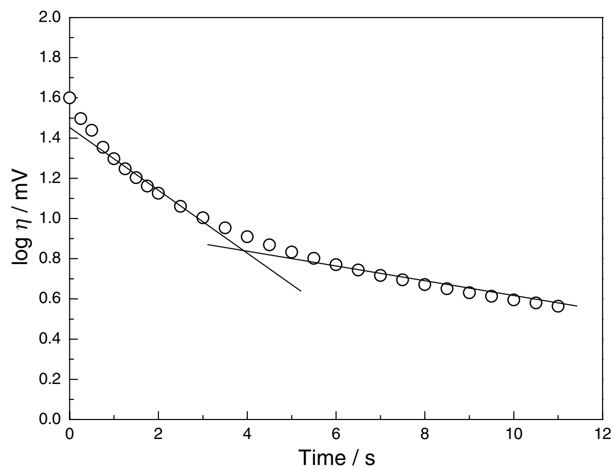

Fig. 8. Decay curve measured on corroding steel in concrete. Plot of log (overpotential) vs time.

experimental points and to deduce from it R_t values that concord with the corrosion status of the tested specimens. Unfortunately, the interest that may exist in using the R_t/CPE/W circuit in the analysis of data is confronted by the complexity of the mathematical treatment, which is much greater than with the simplified Randles circuit traditionally used to represent the behaviour of the steel–concrete interface.

This problem is more serious in the time domain than in the frequency domain, since some of the impedance data analysis programmes existing in the literature may be used in the latter domain [20–23]. In contrast, in the time domain the traditional methods for analysing transients are not exactly applicable to the R_t/CPE/W circuit due to the effect of the CPE. The frequency with which the exponent β of the CPE takes values quite lower than unity emphasises the role of this element in the analysis of data. The methods proposed by Sagüés et al. [16] and Birbilis et al. [17] of direct analysis of the response in the time domain may be useful, provided that the coefficient σ for the diffusion is negligible compared with the value of R_t. Of a more general applicability are, in principle, the methods based on the Laplace and Fourier transformations of transient data from the time domain into the frequency domain, as described by Glass [24] and Cui and Yan [19], and the direct method of Feliu et al. [18].

Although calculation procedures for analysing the data obtained in the time domain are not therefore lacking, the treatments are without doubt improvable in many aspects, such as the exactitude of the estimations, adaptability to different situations, computational efficiency, etc. There is special practical interest in cutting the time for performing the calculations, in such a way that the results are quickly and easily obtained by today's computerised equipment. It is undoubtedly justified to continue to dedicate efforts to these questions.

5. Accuracy achievable in the determinations

It is underlined that one of the advantages of having an appropriate model of the steel–concrete system is the possibility of carrying out studies of the quality of the information that is extracted from the experimental data. The question of the precision achievable in the determinations of the model's parameters always arouse the maximum attention. In our case, this interest refers mainly to the parameters that are related with the corrosion rate, such as the values of R_t and the (apparent) time constant of the corrosion process, i.e. the R_t. Y_o product.

In general, the precision with which the parameters of a model may be determined from the response to an electric signal depends on many factors, such as the suitability of the model to the system under study (errors due to an incorrect model), quality of the experimental data (systematic errors, noise levels, etc.), amount of information analysed (e.g. pulse duration and sampling time), suitability of calculation method to the model used and to the type of signal applied. Even in the event that all of these errors were minimal, the model's very structure represents an additional source of imprecision. We believe that it is of interest to refer to this aspect in the paper for the special case of the R_t/CPE/W model chosen to simulate the steel–concrete system.

The influence of a given parameter in the overall response of a model depends on the relative importance that it has in relation to the other parameters that together define the model. The less sensitive the model's response to a particular parameter, the more imprecise, in principle, its determination will be. The signal/response transfer function allows information to be obtained on the individual and combined effect of a model's parameters. The transfer function G (s) for the steel–concrete interface according to model R_t/CPE/W is deduced from Equation (A.2) given in the Appendix. Replacing jω by the Laplace variable s and omitting the term R_Ω we obtain:

$$G(s) = \frac{x_1(s^{0.5} + x_3)}{(s^{0.5} + x_3)(s^\beta + x_2) - x_2 x_3} \tag{4}$$

in which the variables x_1, x_2, and x_3 are combinations of the parameters R_1, Y_o, and σ:

$$x_1 = 1/Y_o, \tag{5}$$

$$x_2 = 1/Y_o R_t, \tag{6}$$

$$x_3 = \sqrt{2}\sigma/R_t. \tag{7}$$

The transfer function (Equation 4) can give rise to simpler mathematical relations when x_2 and x_3 take

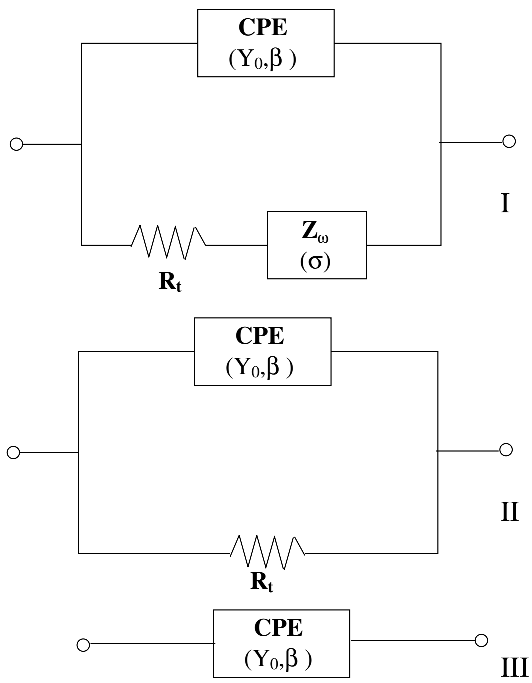

Fig. 9. Participation of parameters Y_o, β, R and σ in the system's response for extreme cases.

certain values. In these circumstances the influence of some model's parameters on the response is negligible, which means that they cannot be reliably estimated from the analysis of the data recorded at the system's entry and exit. Therefore, it is of interest to characterise these cases. The first one, in which simplifications of Equation 4 occur, is when the product $x_2 x_3 \rightarrow 0$, and Equation 4 reduces to equation:

$$\hat{G}(s) = \frac{x_1}{s^\beta + x_2}. \tag{8}$$

This equation coincides with the transfer function of model II in Figure 9 which is a simplification of model I. Thus, for sufficiently small values of the product $x_2 x_3$ the responses of the models I and II practically coincide. In this case the simplification of using model II, which does not contemplate the diffusion effect and whose mathematical treatment is much simpler, would be justified to extract information on the steel–concrete interface.

A second special case is when $x_2 \rightarrow 0$, and Equation 4 reduces to

$$\hat{G}(s) = \frac{x_1}{s^\beta} \tag{9}$$

which coincides with the transfer function of model III in Figure 9. In this case the responses of models I and III will be practically equal, and the simplification of using model III instead of model I would be justified. There is a third case which is when $x_3 \rightarrow \infty$. Then $s^{0.5} + x_3 \sim x_3$ and replacing in (4) we again reach Equation 9.

The three aforementioned cases represent asymptotic behaviours. To define the regions in the $x_2 - x_3$ plane in which the above models are good approximations of the general model (Equation 4), use will be made of a technique that is very well known in the field of the modelling and identification of systems [25], which is based on the comparison of the frequency response of the general model with the responses of its simplifications. According to this technique, the degree of similarity between two transfer functions $G(s)$ and $\hat{G}(s)$ may be quantified according to the expression:

$$J = \frac{1}{2\pi}\int_{-\infty}^{\infty} \left[G(j\omega) - \hat{G}(j\omega)\right]\left[G(j\omega) - \hat{G}(j\omega)\right]^* d\omega, \tag{10}$$

where * denotes conjugate complex. If the value of this integral is smaller than a bound value ε (to be defined) then it can be assured that G and $\hat{G}$ present similar dynamics. It should be mentioned that this integral has also an interpretation in the time domain, since according to Parseval theorem [26]:

$$J = \int_0^{\infty} e^2(t)\,dt,$$

where $e(t)$ is the difference between the responses of the systems G and $\hat{G}$ to a Dirac type pulse input [27]. An alternative function to Equation 10 to quantify the degree of similitude between transfer functions is Equation 11:

$$J = \frac{1}{2\pi}\int_{-\infty}^{\infty} \left[\frac{G(j\omega) - \hat{G}(j\omega)}{G(j\omega)}\right]\left[\frac{G(j\omega) - \hat{G}(j\omega)}{G(j\omega)}\right]^* d\omega\varepsilon, \tag{11}$$

where now the relative difference between transfer functions in the frequency domain is measured.

The bound ε has been selected after several simulations of frequency responses and depending on the desired degree of approximation. To define the aforementioned regions on the x_2–x_3 plane (Figures 10–12) a value of $\varepsilon = 0.01$ has been selected in this work. This value is extremely conservative, and if two transfer functions, as $G(s)$ in Equation 4 and $\hat{G}(s)$ in Equation 8 or 9, satisfy the inequality (11) they may be considered to be equivalent transfer functions for the purposes of this discussion.

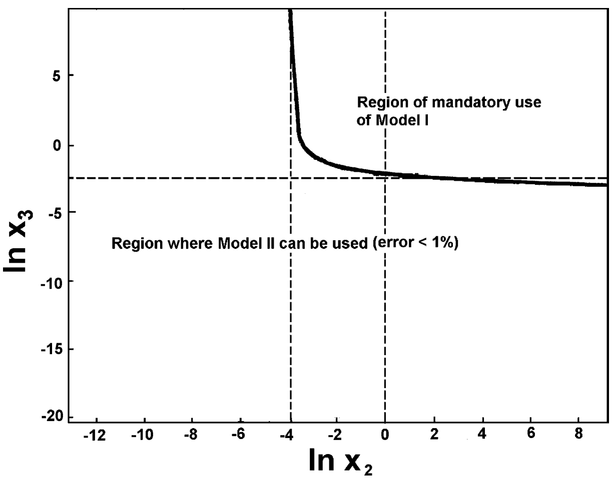

Fig. 10. Sensitivity boundary between the region of mandatory use of model I and region of possible replacement by model II.

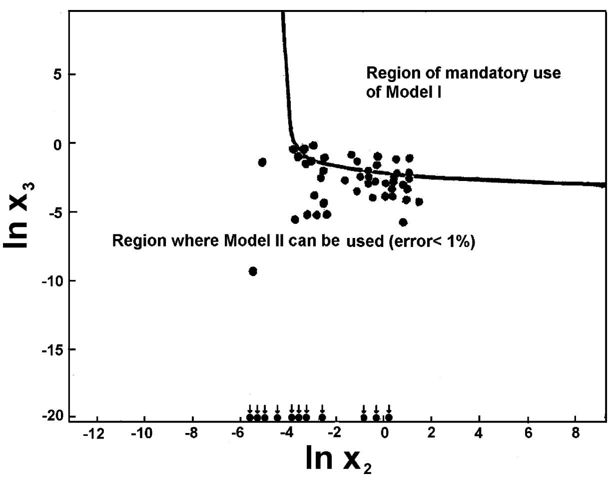

Fig. 11. Ln x_2/ln x_3 diagram showing the position of the points calculated from the experimental results.

Similarity regions have been obtained for β values between 0.55 and 0.95, with β varying in 0.05 steps. In these cases it has been possible to calculate the integral of Equation 11 analytically, giving rise to two families of curves: one for approach given by Equation 8 and another for approach given by Equation 9. The regions have been defined in a conservative way like the respective enveloping lines of these two families of curves.

The boundary corresponding to approach in Equation 8 is shown in Figure 10. This boundary separates the model I compliance region (upper right) (i.e. when there is an important diffusion effect) from the model II compliance region, in which diffusion does not intervene. In general, the smaller the value of $\sigma/R_t = (x_3/\sqrt{2})$, the easier the response will be situated in the region of insensitivity to σ, in which, the estimations of σ are unsure.

It is illustrative to apply the above criteria to steel reinforcements for situations representative of the states of active corrosion and of passivity, with typical values of τ_a ($= Y_o R_t$) of 1 s^β for active steel and of 50 s^β for passive steel. If $\tau_a = 1$ s^β (i.e., $\ln x_2 = 0$), the sensitivity boundary in the diagram of Figure 10 is situated at $\ln x_3 = -2.2$, i.e. $\sigma/R_t = 0.078$ $s^{-0.5}$. Thus, whenever the σ/R_t ratio is below this value it will not be possible to reliably calculate the value of σ. On the other hand, if $\tau_a = 50$ s^β (i.e., $\ln x_2 = -3.9$), this diagram predicts a response that is practically independent of the diffusion for any value of the σ/R_t ratio, and therefore the impossibility in general of making also reliable estimations of σ.

The results obtained by the authors over some 5 years of experimentation with reinforced concrete beams and slabs [10–12, 18] seem to corroborate, in most instances, the idea of a minor effect of diffusion in the steel–concrete system's response. The corrosion parameters which were extracted from the potential-time transients by means of the program in [18] permitted to calculate the coordinates $\ln x_2$ and $\ln x_3$ that determine the position of the points inserted in the diagram in Figure 11. It is important to observe that most of these points (close to 75%) are situated in the region of a possible use of model II, in which diffusion practically does not affect the system's response. It would not therefore be surprising if the simplification of replacing model I with model II were often valid in laboratory and field measurements. In this case, the calculation methods that ignore the diffusion effect, as those of Sagüés et al. [16] and Birbilis et al. [17], would be perfectly justified.

When the impedance of the branch that includes R_t and Z_w is much greater than that of the branch formed by the CPE in model I in Figure 9, the circuit's response would basically be due to the sole action of the CPE, as in model III in Figure 9. In these circumstances it is useless to hope to achieve reliable estimations of σ or of R_t.

Figure 12 plots together the sensitivity boundaries between models I, II and III. The field of the general diagram is now divided into four regions: region A, in which it is necessary to use model I in the numeric analysis; region B, in which the replacement of model I by model II is justified within a 1% error; region C, where the replacement of model I by model II or by model III is justified within a 1% error; and region D, where the replacement of model I by model III is justified within a 1% error. In region A, the model's response is "sensitive" to all the parameters in model I, which could be calculated with an estimable degree of reliability. In region B, the model's response continues to be sensitive to the parameters Y_o, β and R_t, but hardly to σ, for which reason the latter cannot be determined with security. In regions C and D only the parameters Y_o and β seem to significantly influence the model's response, and a precise estimation of R_t and σ is not possible. Naturally, it would be appropriate to bear in mind all of these limitations when extracting information on the steel–concrete system modelled by the R_t/CPE/W circuit.

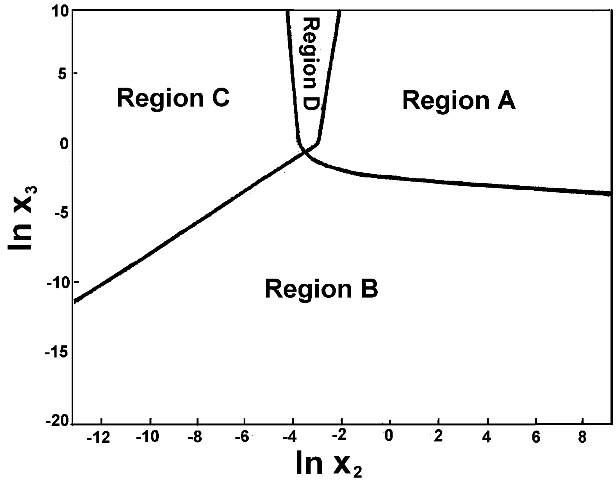

Fig. 12. Representation of conditions (values x_2 and x_3) in which the replacement of model I by models II and III is justified.

6. Conclusions

Experimental evidence is shown in favour of using a modified Randles circuit characterised by a parallel combination of a constant phase element and a charge transfer resistance in series with a Warburg element to model the steel–concrete interface. The availability of the appropiate computational algorithm for fitting the response of this circuit to the experimental data has enabled us to check the suitability of the given model to interpret the corroding behaviour of steel reinforcements. In this respect, it is shown that the charge transfer parameter of the said model gives reliable information on the steel corrosion rate.

The effect of the model structure on the precision with which model parameters can be determined has been also considered. Information on the individual and combined effect of the model parameters is derived from consideration of the signal/response transfer function.

On the basis of this treatment, diagrams have been constructed indicating in which circumstances some parameters, or combinations of them, will have a predominant or negligible effect on the model response and therefore they will be precisely determined or not. In particular, the idea of a minor effect of diffusion in the system response seems to be valid for most measurements of steel corrosion in concrete.

Appendix A

Calculation of the parameters of the $R_t/CPE/W$ circuit from the response to a galvanostatic pulse

The impedance of the R_t/CPE/W circuit (Figure 1(d)) used to represent the steel–concrete system is given by the equation:

$$\frac{u(\omega)}{i(\omega)} = Z(\mathrm{j}\omega) = R_\Omega + \frac{R_t(\mathrm{j}\omega)^{0.5} + \sigma\sqrt{2}}{Y_0(\mathrm{j}\omega)^\beta\left[R_t(\mathrm{j}\omega)^{0.5} + \sigma\sqrt{2}\right] + (\mathrm{j}\omega)^{0.5}}, \qquad (A.1)$$

where $(i\omega)$ = current that enters the circuit and $u(\omega)$ = voltage across it; R_Ω = ohmic resistance of the circuit; and $R_{t,\sigma}, Y_o$ have been defined previously [18].

This expression can be rearranged as

$$Z(\mathrm{j}\omega) = R_\Omega + \frac{x_1\left[(\mathrm{j}\omega)^{0.5} + x_3\right]}{\left[(\mathrm{j}\omega)^{0.5} + x_3\right]\left[(\mathrm{j}\omega)^\beta + x_2\right] - x_2x_3}, \qquad (A.2)$$

where x_1, x_2, and x_3 have also been defined previously.

The system response to a galvanostatic pulse is obtained from the inverse Laplace transform of the product of the transfer function (which is obtained from (A.2) by replacing jω with the Laplace variable s) and the Laplace transforms of the input signal, which is:

$$I(s) = I_0\frac{1 - \mathrm{e}^{-Ls}}{s}, \qquad (A.3)$$

where I_o is the amplitude of the pulse and L is its width. The calculation of the inverse Laplace transform of the product is very complicated because of the fractional terms, whose inverse Laplace transform are summation of series of infinite terms. The solution has been based on a discretised approximation of the differential operator [18].

A search procedure has been implemented in the analysis program which minimises the least squared error D between the simulated voltage u'_k and the measured data u_k:

$$D(\beta, x_1, x_2, x_3, R_s) = \sum_{k=0}^{N-1}\left(u_k - u'_k\right)^2, \qquad (A.4)$$

where N is the number of voltage measurements. Once the values of β, x_1, x_2, x_3, and R_s have been obtained the calculation of Y_o, R_t and σ is immediate.

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